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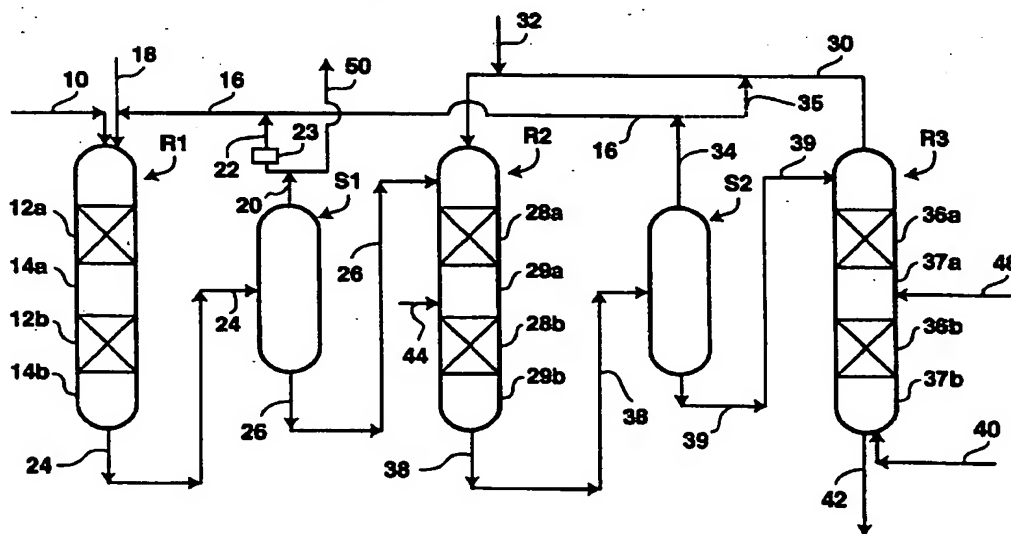
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(54) Title: **LOW SULFUR/LOW AROMATICS DISTILLATE FUELS**



(57) Abstract: A distillate fuel composition boiling in the range of about 190 °C to 400 °C with a T10 point greater than 200 °C, an API gravity less than 43, a sulfur level of less than about 50 wppm, a total aromatics content of about 5 to 15 wt. %, a polynuclear aromatics content of less than about 1.5 wt. %, wherein the ratio of total aromatics to polynuclear aromatics is greater than about 11.

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LOW SULFUR/LOW AROMATICS DISTILLATE FUELS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This is a Continuation-in-Part of USSN 09/457,434 filed December 7, 1999, which claims priority from U.S. Provisional Patent Application No. 60/111,346, filed December 8, 1998.

FIELD OF THE INVENTION

[0002] The present invention relates to a distillate fuel composition boiling in the range of about 190°C to 400°C, and having a sulfur level of less than about 50 wppm, a total aromatics content of about 5 to 15 wt.%, a polynuclear aromatics content of less than about 1.5 wt.%, a total aromatics to polynuclear aromatics ratio of greater than about 11, a T10 boiling point greater than 200°C and an API gravity less than 43.

BACKGROUND OF THE INVENTION

[0003] Diesel fuels are used widely in automotive transport largely due to their high fuel economy. However, one of the problems when such fuels are burned in internal combustion engines is the pollutants in the exhaust gases that are emitted into the environment. For instance, some of the most common pollutants in diesel exhausts are oxides of nitrogen (hereafter abbreviated as "NOx"), particulate matter (including *inter alia* soot, adsorbed hydrocarbons and sulfates), unburned hydrocarbons, and to a lesser extent carbon monoxide. Also, sulfur dioxide emissions from diesel fuel exhaust gases are becoming increasingly a problem due to their affinity with after-treatment devices designed to reduce NOx and particulate emissions, thereby adversely affecting the functioning efficiency. The oxides of sulfur have been reduced considerably by reducing the sulfur levels in the diesel

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itself through refining operations such as by hydrodesulfurization. However, further advances are required to meet increasingly demanding worldwide legislation for progressively lower diesel powered vehicle exhaust emissions, especially NOx and particulate matter. An established trade-off exists between the two pollutants, i.e. NOx and particulate matter, whereby an increase in one leads to a decrease in the other, for a given engine and operating conditions.

[0004] A typical example of such a scenario is U.S. 5,792,339 in which a diesel oil composition comprising 250-495 wppm sulfur, 5-8.6 wt. % of polynuclear aromatics (PNAs) and 10-23.9 wt. % total aromatics is disclosed. At the same time, further advances in sulfur-sensitive after-treatment technology have led to increasing demand for lower levels of sulfur in diesel fuels.

[0005] There are a variety of analytical techniques that have been reported for measurement of total aromatics and polynuclear aromatics. In the discussion and claims that follow, aromatics and PNAs are measured by high performance liquid chromatography (HPLC) as defined by test number IP 391/95, unless otherwise indicated. IP391/95 is described in "IP Standard Methods for Analysis and Testing of Petroleum & Related Products, and British Standard 2000 Parts," 58th edition, February 1999. This publication is incorporated herein by reference. Boiling range distillation determinations were preformed via gas chromatography according to ASTM D2887 providing the temperature at which 10% of the fuel was recovered (T10) and the temperature at which 95% of the fuel was recovered (T95).

[0006] Hydrodesulfurization processes that reduce PNAs typically reduce monocyclic aromatics as well resulting in higher than desired hydrogen consumption. Legislation requiring reduced sulfur content is also anticipated. For example, proposed sulfur limits for distillate fuels to be marketed in the European Union for the year 2005 is 50 wppm or less. Further, the maximum allowable total

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aromatics level for California Air Resources Board (CARB) reference diesel and Swedish Class I diesel are 10 and 5 vol.%, respectively. Further, the CARB reference fuels allows no more than 1.4 vol.% polyaromatics (PNAs). Also, in Europe, starting in 2000, a limit of polynuclear aromatic content in diesel fuel has been set at 11% by weight but no limit has been set for the total aromatic content (including monocyclic aromatics) of the fuel. Consequently, much work is presently being done in the hydrotreating art because of these proposed regulations.

[0007] Hydrotreating, or in the case of sulfur removal, hydrodesulfurization, is well known in the art and typically requires treating the petroleum streams with hydrogen in the presence of a supported catalyst at hydrotreating conditions. The catalyst is usually comprised of a Group VI metal with one or more Group VIII metals as promoters on a refractory support. Hydrotreating catalysts that are particularly suitable for hydrodesulfurization, as well as hydrodenitrogenation, generally contain molybdenum or tungsten as the Group VI metal on alumina support promoted with cobalt, nickel, iron, or a combination thereof as the Group VIII metal. Cobalt promoted molybdenum on alumina catalysts are most widely used when the limiting specifications are hydrodesulfurization, while nickel promoted molybdenum on alumina catalysts are the most widely used for hydrodenitrogenation, partial aromatic saturation, as well as hydrodesulfurization.

[0008] Much work is also being done to develop more active catalysts and to improve reaction vessel designs in order to meet the demand for more effective hydroprocessing processes. Various improved hardware configurations have been suggested. One such configuration is a co-current design where feedstock flows downwardly through successive catalyst beds and treat gas, which is typically a hydrogen-containing treat gas, also flows downwardly, co-current with the feedstock. Another configuration is a countercurrent design wherein the feedstock flows downwardly through successive catalyst beds counter to upflowing treat gas,

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which is typically a hydrogen-containing treat-gas. The downstream catalyst beds, relative to the flow of feed, can contain high performance, but otherwise more sulfur sensitive catalysts because the upflowing treat gas carries away heteroatom components, such as H₂S and NH₃, that are deleterious to sulfur and nitrogen sensitive catalysts.

[0009] Other process configurations include the use of multiple reaction stages, either in a single reaction vessel, or in separate reaction vessels. More sulfur sensitive catalysts can be used in the downstream stages as the level of heteroatom components becomes successively lower. In this regard, European Patent Application 93200165.4 teaches a two-stage hydrotreating process performed in a single reaction vessel.

[0010] Distillate fuel compositions are taught that meet some of the low emissions requirements. For example, U.S. Patent No. 5,389,111 teaches a diesel fuel composition having an aromatics content in the range from about 13 to 20 wt.%, a cetane number from about 54 to 60, which cetane number and aromatics content being within a certain area defined in Figure 1 of that patent. U.S. Patent No. 5,389,112 teaches a low emissions diesel fuel composition having an aromatics content in the range of about 14.3 to 19.7 wt.%, a cetane number from about 53.4 to 60.8, which cetane number and aromatics content falls within a certain area of Figure 1 of that patent.

[0011] While distillate fuel compositions exist that produce lower levels of emissions than years past, there is still a need in the art for fuels with ever lower emissions levels that are needed to meet the ever stricter environmental regulations.

[0012] It has now been found that by controlling the amount of sulfur, PNAs and total aromatics in the diesel fuel within specific limits, the amount of NO_x and particulates emitted from exhausts can be synergistically reduced.

SUMMARY OF THE INVENTION

[0013] In accordance with the present invention there is provided a distillate fuel composition boiling in the range of about 190°C to 400°C with a T10 point greater than 200°C, an API gravity less than 43, a sulfur level of less than about 50 wppm, a total aromatics content of about 5 to 15 wt.%, a polynuclear aromatics content of less than about 1.5 wt.%, wherein the ratio of total aromatics to polynuclear aromatics is greater than about 11.

[0014] In a preferred embodiment of the present invention the sulfur level is less than about 25 wppm.

10 [0015] In another preferred embodiment of the present invention the total aromatics content is from about 10 to 15 wt.%.

[0016] In yet another preferred embodiment of the present invention the polynuclear aromatics content is less than about 1.0 wt.%.

15 [0017] In another preferred embodiment of the present invention, the T10 boiling point is greater than about 200°C.

[0018] In another preferred embodiment of the present invention, the API gravity is less than 43.

[0019] In still another preferred embodiment of the present invention the ratio of total aromatics to polynuclear aromatics is greater than about 14.

20 [0020] In another preferred embodiment, the fuel is employed in a compression ignition (e.g., diesel) engine, preferably in order to abate NOx and particulate emissions therefrom. More preferably, the fuel is employed in an automotive diesel engine.

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[0021] In another embodiment, the invention is a fuel composition comprising a distillate boiling in the range of about 190°C to 400°C with a T10 point greater than 200°C, an API gravity less than 43, a sulfur level of less than about 50 wppm, a total aromatics content of about 5 to 15 wt.%, a polynuclear aromatics content of less than about 1.5 wt.%, wherein the ratio of total aromatics to polynuclear aromatics is greater than about 11, to which is added at least one of (i) one or more lubricity aid, (ii) one or more viscosity modifier, (iii) one or more antioxidant, (iv) one or more cetane improver, (v) one or more dispersant, (vi) one or more cold flow improver, (vii) one or more metals deactivator, (viii) one or more corrosion inhibitor, (ix) one or more detergent, and (x) one or more distillate or upgraded distillate.

BRIEF DESCRIPTION OF THE FIGURES

[0022] Figure 1 hereof shows one preferred process scheme for producing the distillate fuel compositions of the present invention. This process scheme shows two hydrodesulfurization stages and one aromatics saturation stage. Also shown in this figure is hydrogen-containing treat gas being cascaded from the downstream reaction stages to the upstream reaction stages.

[0023] Figure 2 hereof is a plot of the data relating to some properties of the products produced by the practice of this invention. Total aromatics content is plotted versus the ratio of total aromatics to polynuclear aromatics.

DETAILED DESCRIPTION OF THE INVENTION

[0024] Feedstocks suitable for producing the low emissions distillate fuel compositions of this invention are those petroleum based feedstocks boiling in the distillate range and above. Such feedstocks typically have a boiling range from

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about 190 to about 400°C, preferably from about 200 to about 370°C. These feedstocks usually contain greater than about 3,000 wppm sulfur. Non-limiting examples of such feedstocks include virgin distillates, light cat cycle oils, light coker oils, etc. It is highly desirable for the refiner to upgrade these types of feedstocks by removing as much of the sulfur as possible, as well as to saturate aromatic compounds.

[0025] It is not critical how the distillate fuel compositions are produced.

One preferred process for producing the fuel products of the present invention is illustrated in Figure 1 hereof. The process scheme shown in Figure 1 hereof offers an improvement over the prior art by using only once-through hydrogen treat gas in at least one of the stages. For purposes of discussion, the first hydrodesulfurization stage will reduce the levels of both sulfur and nitrogen, with sulfur levels being less than about 1,000 wppm, preferably to less than about 500 wppm. The second hydrodesulfurization stage will reduce sulfur levels to less about 100 wppm. The third stage, the aromatics hydrogenation stage, will saturate a substantial amount of the aromatics. In the practice of this invention the hydrogen in the treat gas reacts with impurities to convert them to H₂S, NH₃, and water vapor, which are removed as part of the vapor effluent, and it also saturates olefins and aromatics.

[0026] Miscellaneous reaction vessel internals, valves, pumps,

thermocouples, and heat transfer devices etc. are not shown for simplicity. Figure 1 shows hydrodesulfurization reaction vessel R1 which contains reaction zones 12a and 12b, each of which is comprised of a bed of hydrodesulfurization catalyst. It will be understood that a this reaction stage can contain only one reaction zones or two or more reaction zones. It is preferred that the catalyst be in the reactor as a fixed bed, although other types of catalyst arrangements can be used, such as slurry or ebullating beds. Downstream of each reaction zone is a non-reaction zone, 14a

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and 14b. The non-reaction zone is typically void of catalyst, that is, it will be an empty section in the vessel with respect to catalyst. Although not shown, there may also be provided a liquid distribution means upstream of each reaction stage or catalyst bed. The type of liquid distribution means is believed not to limit the practice of the present invention, but a tray arrangement is preferred, such as sieve trays, bubble cap trays, or trays with spray nozzles, chimneys, tubes, etc. A vapor-liquid mixing device (not shown) can also be employed in non-reaction zone 14a for the purpose of introducing a quench fluid (liquid or vapor) for temperature control.

[0027] The feedstream is fed to reaction vessel R1 via line 10 along with a hydrogen-containing treat gas via line 16 that is cascaded from second hydrodesulfurization reaction stage R2. The term "cascaded", when used in connection with a treat gas, means a stream of treat gas is separated from the vapor effluent of a first reaction stage and then conducted to the inlet of a second reaction stage without passing through a compressor. The second reaction stage may be upstream or downstream of the first reaction stage with respect to liquid flow. In other words, the relative reaction conditions in the first and second reaction stages and associated separation zones are regulated so that the treat gas in the vapor phase effluent from the first stage naturally flows to the second stage, without the need to increase the pressure of the treat gas in the first stage's vapor phase effluent.

[0028] Though not required, all or a portion of the hydrogen-containing treat gas may also be conducted to hydrodesulfurization reaction stage R1 via line 18. This additional hydrogen-containing treat gas will typically be cascaded or otherwise obtained from another refinery process unit, such as a naphtha hydrofiner. The vapor effluent from S1 may be (i) recycled via lines 20, 22, and 16, (ii) conducted away from the process via line 50, or (iii) used in a combination of (i) and (ii). The term "recycled" when used herein regarding hydrogen treat gas is

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meant to indicate a stream of hydrogen-containing treat gas separated as a vapor effluent from one stage that passes through a gas compressor 23 to increase its pressure prior to being sent to the inlet of a reaction stage. It should be noted that the compressor will also generally include a scrubber to remove undesirable species such as H₂S from the hydrogen recycle stream. The feedstream and hydrogen containing treat gas pass, co-currently, through the one or more reaction zones of hydrodesulfurization stage R1 to remove a substantial amount of the heteroatoms, preferably sulfur, from the feedstream. It is preferred that the first hydrodesulfurization stage contain a catalyst comprised of Co-Mo, or Ni-Mo on a refractory support.

[0029] The term "hydrodesulfurization" as used herein refers to processes wherein a hydrogen-containing treat gas is used in the presence of a suitable catalyst which is primarily active for the removal of heteroatoms, preferably sulfur, and nitrogen, and for some hydrogenation of aromatics. Suitable hydrodesulfurization catalysts for use in the reaction vessel R1 in the present invention include conventional hydrodesulfurization catalyst such as those that are comprised of at least one Group VIII metal, preferably Fe, Co or Ni, more preferably Co and/or Ni, and most preferably Co; and at least one Group VI metal, preferably Mo or W, more preferably Mo, on a relatively high surface area refractory support material, preferably alumina.. Other suitable hydrodesulfurization catalyst supports include refractory oxides such as silica, zeolites, amorphous silica-alumina, and titania-alumina. Additives such as P can also be present. It is within the scope of the present invention that more than one type of hydrodesulfurization catalyst be used in the same reaction vessel and in the same reaction zone. The Group VIII metal is typically present in an amount ranging from about 2 to 20 wt.%, preferably from about 4 to 15%. The Group VI metal will typically be present in an amount ranging from about 5 to 50 wt.%, preferably from about 10 to 40 wt.%, and more preferably from about 20 to 30

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wt.%. All metals weight percents are based on the weight of the catalyst. Typical hydrodesulfurization temperatures range from about 200°C to about 400°C with a total pressures of about 50 psig to about 3,000 psig, preferably from about 100 psig to about 2,500 psig, and more preferably from about 150 to 500 psig. More preferred hydrogen partial pressures will be from about 50 to 2,000 psig, most preferably from about 75 to 800 psig.

[0030] A combined liquid phase/vapor phase product stream exits hydrodesulfurization stage R1 via line 24 and passed to separation zone S1 wherein a liquid phase product stream is separated from a vapor phase product stream. The liquid phase product stream will typically be one that has components boiling in the range from about 190°C to about 400°C, but will not have an upper boiling range greater than the feedstream. The vapor phase product stream is collected overhead via line 20. The liquid reaction product from separation zone S1 is passed to hydrodesulfurization stage R2 via line 26 and is passed downwardly through the reaction zones 28a and 28b. Non-reaction zones are represented by 29a and 29b.

[0031] Hydrogen-containing treat gas is introduced into reaction stage R2 via line 30 that is cascaded from aromatics hydrogenation stage R3 and is passed cocurrent with the feedstock. As discussed, the term "cascaded" means that treat gas flows from a downstream reaction stage, such as the hydrogenation stage, to an upstream stage that is at the same or lower pressure, and thus there is no need for the gas to be compressed. Though not required, all or a portion of the treat gas may be added into R2 via line 32, which additional treat gas may be from another refinery process unit, such as a naphtha hydrofiner. It is preferred that the rate of introduction of hydrogen contained in the treat gas be less than or equal to 3 times the chemical hydrogen consumption of this rate, more preferably less than about 2 times, and most preferably less than about 1.5 times. The feedstream and hydrogen-containing treat gas pass, co-currently, through the one or more reaction

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zones of hydrodesulfurization stage R2 to remove a substantial amount of remaining sulfur, preferably to a level wherein the feedstream now has less than about 50 wppm sulfur, more preferably less than about 25 wppm sulfur.

[0032] Suitable hydrodesulfurization catalysts for use in the reaction vessel

5 R2 in the present invention include conventional hydrodesulfurization catalyst such as those described for use in R1. Noble metal catalysts can also be employed, which is preferably selected from Pt and Pd or a combination thereof. Pt, Pd or the combination thereof is typically present in an amount ranging from about 0.5 to 5 wt.%, preferably from about 0.6 to 1 wt.%. Typical hydrodesulfurization
10 temperatures range from about 200°C to about 400°C with a total pressures of about 50 psig to about 3,000 psig, preferably from about 100 psig to about 2,500 psig, and more preferably from about 150 to 1,500 psig. More preferred hydrogen partial pressures will be from about 50 to 2,000 psig, most preferably from about 75 to 1,000 psig. Preferably, R2 outlet pressure ranges from about 500 to about 1000
15 psig.

[0033] The reaction product from second hydrodesulfurization stage R2 is passed via line 38 to second separation zone S2 wherein a vapor product, containing hydrogen, is recovered overhead and passed to either, or both, of hydrodesulfurization stage R1 via lines 34 and 16, or for recycle via lines 34 and 35.

20 Alternatively, all or a portion of S2's vapor product may be conducted away from the process. The liquid fraction is passed to aromatics hydrogenation stage R3, via line 39 where it flows downward through reaction zones 36a and 36b. Non-reaction zones, similar to those in R2 and R3, are represented by 37a and 37b. Prior to being passed downwardly through the reaction zones of R3, said liquid fraction can first
25 be contacted in a stripping zone (not shown) to remove entrapped vapor components from the liquid stream. For example, as the liquid product stream flows through the stripping zone, it is contacted by upflowing hydrogen-containing treat gas under

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conditions effective for transferring at least a portion of the feed impurities (H_2S and NH_3) from the liquid to the vapor. It is preferred that at least about 80%, more preferably at least about 90% of the remaining H_2S and NH_3 will be removed from the downflowing liquid stream. The contacting means comprises any known vapor-liquid contacting means, such as rashig rings, berl saddles, wire mesh, ribbon, open honeycomb, gas-liquid contacting trays, such as bubble cap trays and other devices, etc. It is within the scope of this invention that the stripping zone may be part of reaction vessel R3 or it may be a separate vessel. It is to be understood that although the figure hereof shows the hydrogenation stage operated in countercurrent mode wherein treat gas flows countercurrent to the flow of feedstock, it is understood that the hydrogenation stage can be operated in cocurrent mode as well.

[0034] Fresh hydrogen-containing treat gas is introduced into reaction stage R3 via line 40 and is passed in an upward direction counter to the flow of liquid reaction product. The treat gas rate is preferably from about 400 to 1,200 scf/bbl (standard cubic feet per barrel), more preferably from about 500 to 1,000 scf/bbl. The introduction of clean treat gas (gas substantially free of H_2S and NH_3) allows reaction stage R3 to be operated more efficiently owing to a reduction in the activity suppression effects on the catalyst exerted by H_2S and NH_3 and an increase in H_2 partial pressure. This type of multi-stage operation is particularly attractive for very deep removal of sulfur and nitrogen or when a more sensitive catalyst (i.e., hydrocracking, aromatic saturation, etc) is used in the second reactor. Another advantage of the present invention is that the treat gas rate is relatively low compared with more conventional processes. The use of relatively low treat gas rates is primarily due to the use of previously hydrotreated distillate feedstocks. Further efficiencies are gained by not requiring recycle of treat gas. In other words, in one embodiment the treat gas used in R3 is a once-through treat gas.

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[0035] The liquid stream and treat gas are passed countercurrent to each other through one or more catalyst beds, or reaction zones, 36a and 36b. The resulting liquid product stream exits reaction stage R3 via line 42, and a hydrogen-containing vapor product stream exits reaction stage R3 and is cascaded to reaction stage R2 via line 30. The catalyst used in the reaction zones of this second reaction stage can be any suitable aromatics saturation catalyst. Non-limiting examples of aromatics hydrogenation catalysts include nickel, cobalt-molybdenum, nickel-molybdenum, nickel-tungsten, and noble metal containing catalysts. Preferred are the noble metal catalysts. Non-limiting examples of noble metal catalysts include those based on platinum and/or palladium, which is preferably supported on a suitable support material, typically a refractory oxide material such as alumina, silica, alumina-silica, kieselguhr, diatomaceous earth, magnesia, and zirconia. Zeolitic supports can also be used. Such catalysts are typically susceptible to sulfur and nitrogen inhibition or poisoning. The aromatic saturation stage is preferably operated at a temperature from about 40°C to about 400°C, more preferably from about 200°C to about 350°C, at a pressure from about 100 psig to about 3,000 psig, preferably from about 200 psig to about 1,200 psig, and at a liquid hourly space velocity (LHSV) of from about 0.3 V/V/Hr. to about 10 V/V/Hr, preferably from about 1 to 5 V/V/Hr.

[0036] The figure also shows several options. For example, line 44 to R2 and line 46 to R3 can carry a quench fluid that may be either a liquid or a gas. Hydrogen is a preferred gas quench fluid and kerosene is a preferred liquid quench fluid.

[0037] While the reaction stages used in the practice of the present invention are operated at suitable temperatures and pressures for the desired reaction, they are preferably regulated to provide for treat gas cascading from R2 and R3 to R1, and for once-through treat gas in R2. For example, while typical hydroprocessing

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temperatures will range from about 20°C to about 400°C at pressures from about 50 psig to about 3,000 psig, reaction conditions, particularly reaction pressures, will generally be regulated to provide the desired treat gas flow to minimize or preferably eliminate the need for ancillary pressure regulation equipment, such as compressors.

[0038] It is also within the scope of this invention that the hydrogenation stage contain two or more reaction zones operated at different temperatures. That is, at least one of the reaction zones will be operated at a temperature at least 25°C, preferably at least about 50°C cooler than the other zone(s). It is preferred that the last downstream reaction zone, with respect to the flow of feedstock be the reaction zone that it operated at the cooler temperatures.

[0039] For purposes of hydroprocessing and in the context of the present invention, the terms "hydrogen" and "hydrogen-containing treat gas" are synonymous and may be either pure hydrogen or a hydrogen-containing treat gas which is a treat gas stream containing hydrogen in an amount at least sufficient for the intended reaction, plus other gas or gasses (e.g., nitrogen and light hydrocarbons such as methane) which will not adversely interfere with or affect either the reactions or the products. Impurities, such as H₂S and NH₃ are undesirable and, if present in significant amounts, will normally be removed from the treat gas, before it is fed into the R1 reactor. The treat gas stream introduced into a reaction stage will preferably contain at least about 50 vol.% hydrogen, more preferably at least about 75 vol.% hydrogen, and most preferably at least 95 vol.% hydrogen. In operations in which unreacted hydrogen in the vapor effluent of any particular stage is used for hydroprocessing in any stage, there must be sufficient hydrogen present in the fresh treat gas introduced into that stage for the vapor effluent of that stage to contain sufficient hydrogen for the subsequent stage or stages. In one embodiment, all or a portion of the hydrogen required for the first stage hydroprocessing is

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contained in the second stage vapor effluent fed up into the first stage. The first stage vapor effluent will be cooled to condense and recover the hydrotreated and relatively clean, heavier (e.g., C₄+) hydrocarbons.

[0040] The liquid phase in the reaction vessels used in the present invention will typically be comprised of primarily the higher boiling point components of the feed. The vapor phase will typically be a mixture of hydrogen-containing treat gas, heteroatom impurities like H₂S and NH₃, and vaporized lower-boiling components in the fresh feed, as well as light products of hydroprocessing reactions. If the vapor phase effluent still requires further hydroprocessing, it can be passed to a vapor phase reaction stage containing additional hydroprocessing catalyst and subjected to suitable hydroprocessing conditions for further reaction. Alternatively, the hydrocarbons in the vapor phase products can be condensed via cooling of the vapors, with the resulting condensate liquid being recycled to either of the reaction stages, if necessary. It is also within the scope of the present invention that a feedstock which already contains adequately low levels of heteroatoms be fed directly into the reaction stage for aromatic saturation and/or cracking.

[0041] As discussed, the preferred process may be used to form the fuel products of the invention. Such distillate fuel products are characterized as having relatively low sulfur and polynuclear aromatics (PNAs) levels and a relatively high ratio of total aromatics to polynuclear aromatics. Such distillate fuels may be employed in compression-ignition engines such as diesel engines, particularly so-called "lean-burn" diesel engines. Such fuels are compatible with: compression-ignition engine systems such as automotive diesel systems utilizing (i) sulfur-sensitive NO_x conversion exhaust catalysts, (ii) engine exhaust particulate emission reduction technology, including particulate traps, and (iii) combinations of (i) and (ii). Such distillate fuels have moderate levels of total aromatics, reducing the cost of producing cleaner-burning diesel fuel and also reducing CO₂ emissions by

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minimizing the amount of hydrogen consumed in the process. In one embodiment, the distillate compositions of the present invention contain less than about 50 wppm, preferably less than about 25 wppm, more preferably less than about 10 wppm, and most preferably less than about 5 wppm sulfur. They will also have a total aromatics content from about 5 to 15 wt.%, preferably from about 10 to 15 wt.%. The PNA content of the distillate product compositions obtained by the practice of the present invention will be less than about 1.5 wt.%, preferably less than about 1.0 wt.%, and more preferably less than about 0.5 wt.%. In one embodiment, the aromatics to PNA ratio will be at least about 11, preferably at least about 14, and more preferably at least about 17. In another embodiment, the aromatics to PNA ratio ranges from 11 to about 50, preferably from 11 to about 30, and more preferably from 11 to about 20.

[0042] The term PNA is meant to refer to polynuclear aromatics that are defined as aromatic species having two or more aromatic rings, including alkyl and olefin-substituted derivatives thereof. Naphthalene and phenanthrene are examples of PNAs. The term aromatics is meant to refer species containing one or more aromatic ring, including alkyl and olefin-substituted derivatives thereof. Thus, naphthalene and phenanthrene are also considered aromatics along with benzene, toluene and tetrahydronaphthalene. It is desirable to reduce PNA content of the liquid product stream since PNAs contribute significantly to emissions in diesel engines. However, it is also desirable to minimize hydrogen consumption for economic reasons and to minimize CO₂ emissions associated with the manufacture of hydrogen via steam reforming. Thus, the current invention achieves both of these by obtaining a high aromatics to PNA ratio in the liquid product.

[0043] The fuels of the present invention boil in the range of about 190°C to 400°C. Fuels having a ratio of total aromatics/PNAs >11 can be prepared by blending large amounts of lighter materials which contain single ring aromatics, but

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few PNAs. The fuels of the present invention are also distinguished from these in that the T10 boiling point is greater than 200°C and the API gravity is less than 43.

[0044] In one embodiment, the fuels may be combined with other distillate or upgraded distillate. As discussed, the products are compatible with effective amounts of fuel additives such as lubricity aids, cetane improvers, and the like. While a major amount of the product is preferably combined with a minor amount of the additive, the fuel additive may be employed to an extent not impairing the performance of the fuel. While the specific amount(s) of any additive employed will vary depending on the use of the product, the amounts may generally range from 0.05 to 2.0 wt.% based on the weight of the product and additive(s), although not limited to this range. The additives can be used either singly or in combination as desired.

[0045] The following examples are presented to illustrate the present invention and not to be taken as limiting the scope of the invention in any way.

EXAMPLES 1 - 3

[0046] A virgin distillate feed containing from about 10,000 to 12,000 wppm sulfur was processed in a commercial hydrodesulfurization unit (first hydrodesulfurization stage) using a reactor containing both conventional commercial NiMo/ Al₂O₃ (Akzo-Nobel KF842/840) and CoMo/Al₂O₃ (Akzo-Nobel KF-752) catalyst under the following typical conditions: 300-350 psig; 150-180 psig outlet H₂; 75% H₂ treat gas; 500-700 SCF/B treat gas rate; 0.3-0.45 LHSV; 330-350°C.

[0047] The liquid product stream from this first hydrodesulfurization stage was used as feedstream to the second hydrodesulfurization stage, which product

stream is described under the feed properties heading in Table 1 below. The process conditions for this second hydrodesulfurization stage are also shown in the table below. A commercial NiMo catalyst (Criterion C-411 containing 2.6 wt.% Ni and 14.3 wt.% Mo) was used in all of the runs.

[0048] The liquid product stream from this second hydrodesulfurization stage was used as the feed for the aromatics saturation stage. A commercial PtPd catalyst (Criterion Synsat-4) was used in all of the runs. Feed and product properties are shown in the table below.

[0049] Examples 1 - 3 demonstrate that products with less than 50 ppm S can be produced wherein the rate of introduction of hydrogen in the treat gas in the second reaction stage is less than or equal to three times the chemical hydrogen consumption. Examples 1-3 also demonstrate that products with 5-15 wt.% aromatics can be produced having a ratio of total aromatics to PNAs greater than about 11 and a T10 boiling point greater than 200°C.

Table 1

| | Example 1 | Example 2 | Example 3 |
|--|--|--|--|
| Process conditions for second HDS stage | | | |
| T, °C | 332 | 331 | 342 |
| Pressure, psig | 800 | 800 | 800 |
| LHSV | 1.1 | 1.48 | 1.1 |
| Treat gas rate (100% H ₂) , SCF/B | 510 | 441 | 455 |
| Catalyst | Commercial NiMo/Al ₂ O ₃ | Commercial NiMo/Al ₂ O ₃ | Commercial NiMo/Al ₂ O ₃ |
| Feed properties for second HDS stage | | | |
| S, wppm | 345 | 101 | 238 |
| N, wppm | 73 | 51 | 113 |
| API | 35.9 | 35 | 35.3 |
| T95, °C | 367 | 374 | 373 |
| Total aromatics, wt.% (HPLC IP 391/95) | 26.13 | 27.22 | 26.97 |
| PNA, wt.% (HPLC IP 391/95) | 6.09 | 7.71 | 7.9 |
| H content, wt.% | 13.52 | 13.37 | 13.34 |

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| | Example 1 | Example 2 | Example 3 |
|---|-----------|-----------|-----------|
| Product properties from second HDS stage (feed to aromatic saturation stage) | | | |
| S, wppm | 33.8 | 19.1 | 33.5 |
| API | 36.6 | 35.8 | 35.4 |
| Total aromatics, wt.% (HPLC IP 391) | 23.1 | 28.28 | 24.22 |
| PNA, wt.% (HPLC IP 391) | 1.97 | 2.59 | 2.05 |
| Total aromatics/PNA | 11.72 | 10.92 | 11.81 |
| H ₂ consumption, SCF/B | 200 | 175 | 200 |
| H ₂ Treat gas rate/H ₂ consumption for 2nd HDS stage | 2.6 | 2.5 | 2.3 |
| Process conditions for aromatic saturation stage | | | |
| T, °C | 272 | 267 | 287 |
| Pressure, psig | 800 | 800 | 800 |
| LHSV | 2.74 | 2.03 | 2.75 |
| Treat gas rate (100% H ₂), SCF/B | 786 | 613 | 621 |
| Product properties from aromatic saturation stage | | | |
| S, wppm | 9.74 | 8 | 8.95 |
| API | 37.9 | 37.1 | 37.6 |
| T10 °C | 235 | 237 | 235 |
| T95 °C | 366 | 372 | 372 |
| H content, wt.% | 14.12 | 13.94 | 14.02 |
| Total aromatics, wt.% (HPLC IP 391/95) | 8.74 | 14.18 | 10.46 |
| PNA, wt.% (HPLC IP 391/95) | 0.75 | 0.89 | 0.47 |
| Total aromatics/PNA | 11.65 | 15.93 | 22.26 |

COMPARATIVE EXAMPLES A-E

[0050] Comparative Examples A-E are all conventional fuels with less than 50 wppm S. Comparative examples A, B, C and D describe fuels that have total aromatics levels greater than 15 wt.% and all have a ratio of total aromatics to PNAs less than 10, which is outside the range of this invention. Comparative example E is a Swedish Class 1 diesel which has a very low total aromatics level of less than 5 wt.% and a total aromatics to PNA ratio of greater than 25. Products with less than 5 wt.% total aromatics are outside the range of this invention.

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Table 2

| | Comparative Example A | Comparative Example B | Comparative Example C | Comparative Example D | Comparative Example E |
|---|---|---|--|-------------------------------------|--------------------------|
| Reference | Executive Order G-714-007 Of the Calif. Air Resources Board | Executive Order G-714-008 Of the Calif. Air Resources Board | As described in Tosco U.S. 5792339 | U.S. 5389111 and U.S. 5389112 | |
| Product properties | | | | | |
| S, wppm | 33 | 42 | <5 | 44 | 8.95 |
| Total aromatics, vol.% (D1319-84; FIA) | 21.7 | 24.7 | | | |
| PNA, wt.% (D 2425-83; mid-distillate MS) | 4.6 | 4.0 | 1.9 | 2.56 | |
| Total aromatics, wt.% (D 5186; SFC) | | | 19.4 | 16 | 4.06 |
| PNA, wt.% (D 5186; SFC) | | | | | 0.16 |
| Total aromatics/PNA | 4.72 | 6.18 | 10.2 | 6.25 | 25.4 |

- 5 [0051] The area inside the box in Figure 2 defines the products of this invention. The total aromatics/PNA ratio can be greater than 30. Even though Figure 2's abscissa is truncated at 30 for clarity, it should be understood that the total aromatics/PNA ratio may exceed 30. In addition to the total aromatics (5-15 wt.%) and total aromatics/PNA criteria the preferred products of the invention have
- 10 S levels less than about 50 wppm, a T10 boiling point greater than 200 °C, and an API gravity less than 43. The designations "FIA", "MS", and "SFC" are well known in the art as analytical techniques. For example, "FIA" stands for fluorescence indicator analysis, "MS" stands for mass spectrophotometry; and "SFC" stands for supercritical fluid chromatography.

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[0052] Table 3 provides additional comparative examples of distillate fuels that fall outside the range of this invention. These data were obtained from the following publications.

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- 3-1 X. Li et al. "Comparison of the Exhaust Emissions of Diesel Fuels Derived From Oil Sands and Conventional Crude Oil," SAE Technical Paper Series 982487, Oct. 19-22, 1998.
- 5 3-2 B. Martin et al., Influence of Future Fuel Formulations on Diesel Engine Emissions - A Joint European Study," SAE Technical Paper Series 972966, Oct. 13-16, 1997.
- 10 3-3 A. Gerini et al. "Automotive Direct Injection Diesel Engine Sensitivity to Diesel Fuel Characteristics," SAE Technical Paper Series 972963, Oct. 13-16, 1997.
- 15 3-4 T. W. Ryan III et al., "Diesel Fuel Composition Effects on Ignition and Emissions," SAE Technical Paper Series 932735, Oct. 18-21, 1993
- 3-5 M. A. Gonzalez et al., "A Low Emission Diesel Fuel: Hydrocracking Production, Characterization and Engine Evaluations," SAE Technical Paper Series 932731, Oct. 18-21, 1993
- 20 3-6 C. I. McCarthy, "Diesel Fuel Property Effects on Exhaust Emissions from a Heavy Duty Diesel Engine that Meets 1994 Emission Requirements," SAE Technical Paper Series 922267, Oct. 19-22, 1992
- 25 3-7 W. W. Lange, "The Effect of Fuel Properties on Particulates Emissions in Heavy Duty Truck Engines Under Transient Operating Conditions," SAE Technical Paper Series 9212425, Oct. 7-10, 1991

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- 3-8 C. Beatrice et al., "Potentiality of Oxygenated Synthetic Fuel and Reformulated Fuel on Emissions from a Modern DI Diesel Engine," SAE Technical Paper Series 1999-01-3595, Oct. 25-28, 1999
- 5 3-9 N. Mann et al., "Fuel Effects on The Low Temperature Performance of Two Generations of Mercedes-Benz Heavy-Duty Diesel Engines," SAE Technical Paper Series 1999-01-3594, Oct. 25-28, 1999
- 10 3-10 D. A. Kouremenos et al., "Experimental Investigation of the Effect of Fuel Composition on the Formation of Pollutants in Direct Injection Diesel Engines," SAE Technical Paper Series 1999-01-0189, Mar. 1-4, 1999
- 15 3-11 C. Bertoli et al., "The Influence of Fuel Composition on Particulate Emissions of DI Diesel Engines," SAE Technical Paper Series 932733, Oct. 18-21, 1993

[0053] Data reported for the wt.% total aromatics content and PNAs are shown along with the calculated ratio of wt.% aromatics / wt.% PNAs. The analytical test method for measurement of aromatics and PNAs is also indicated

20 along with sulfur content and the T10 boiling point. Fuels #1 - 127 all have an aromatics/PNA ratio less than 11. Fuels # 128 - 134 have a sulfur content greater than 50 wppm. Fuels #135 - 138 have an aromatics content greater than 15 wt.%. Fuels 139 - 150 have an aromatics content less than or equal to 5 wt.%. Fuels # 151-155 have an API gravity greater than or equal to 43. And, Fuels 156 - 158

25 have T10 boiling points less than 200°C. Thus, all of the fuels shown in Table 3 fall outside the range of the fuels of the subject invention.

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Table 3

| <u>Fuel #</u> | <u>Pub. #</u> | <u>Fuel Ref.</u> | <u>API Gravity</u> | <u>T10 °C</u> | <u>Aromatics, wt. %</u> | <u>PNAs, wt. %</u> | <u>Arom./PNA</u> | <u>Anal. Test</u> | <u>S, wppm</u> |
|---------------|---------------|------------------|--------------------|---------------|-------------------------|--------------------|------------------|-------------------|----------------|
| 1 | 3-4 | LSLCO7 | 17.5 | 343.3 | 31.9 | 29.6 | 1.1 | UV | 1100 |
| 2 | 3-4 | LCO5 | 16.8 | 286.7 | 42.7 | 39.4 | 1.1 | UV | 3200 |
| 3 | 3-4 | LCO4 | 18.4 | 268.3 | 60.5 | 55.5 | 1.1 | UV | 4100 |
| 4 | 3-4 | LCO3 | 20.3 | 250.6 | 57.2 | 50.4 | 1.1 | UV | 4500 |
| 5 | 3-4 | LCO6 | 14.6 | 306.1 | 36.4 | 31.5 | 1.2 | UV | 5700 |
| 6 | 3-4 | LCO0 | 17.6 | 246.7 | 43.7 | 37.4 | 1.2 | UV | 2600 |
| 7 | 3-4 | LCO7 | 10.3 | 339.4 | 37.8 | 31.4 | 1.2 | UV | 18500 |
| 8 | 3-4 | LCO2 | 23.2 | 230.6 | 55.2 | 40.8 | 1.4 | UV | 3500 |
| 9 | 3-7 | DD9 | 34.0 | 218.0 | 34.33 | 24.9 | 1.4 | HPLC IP391 | 500 |
| 10 | 3-4 | LSLCO6 | 17.7 | 312.8 | 32.8 | 23.1 | 1.4 | UV | 400 |
| 11 | 3-11 | TAC10 | 39.2 | 213.0 | 13.7 | 9.6 | 1.4 | Mass Spec. | 1050 |
| 12 | 3-4 | SRD3 | 35.3 | 252.2 | 13.3 | 8.9 | 1.5 | UV | 200 |
| 13 | 3-4 | SRD2 | 36.1 | 240.6 | 13.5 | 9 | 1.5 | UV | 100 |
| 14 | 3-4 | SRD7 | 33.2 | 325.0 | 9.3 | 6.2 | 1.5 | UV | 1200 |
| 15 | 3-4 | SRD4 | 35.4 | 267.8 | 12.5 | 8.2 | 1.5 | UV | 300 |
| 16 | 3-4 | LSLCO5 | 19.8 | 283.9 | 34.1 | 22.3 | 1.5 | UV | 100 |
| 17 | 3-4 | SRD5 | 36.0 | 284.4 | 10.9 | 6.9 | 1.6 | UV | 400 |
| 18 | 3-4 | SRD6 | 35.6 | 303.3 | 8.7 | 5.5 | 1.6 | UV | 700 |
| 19 | 3-4 | LCGO7 | 24.1 | 317.2 | 15.2 | 9.6 | 1.6 | UV | 13300 |
| 20 | 3-4 | SRD0 | 35.8 | 241.1 | 11.4 | 7.1 | 1.6 | UV | 500 |
| 21 | 3-4 | LCGO6 | 27.0 | 296.1 | 14.7 | 8.5 | 1.7 | UV | 13200 |
| 22 | 3-4 | LCGO5 | 28.0 | 276.7 | 15.1 | 8.5 | 1.8 | UV | 14800 |
| 23 | 3-7 | DD10 | 41.3 | 214.0 | 8.96 | 5.02 | 1.8 | HPLC IP391 | 400 |
| 24 | 3-4 | LSLCO4 | 21.8 | 261.7 | 36.8 | 20.2 | 1.8 | UV | 0 |
| 25 | 3-4 | LSLCO0 | 22.3 | 222.2 | 35.8 | 19.2 | 1.9 | UV | 300 |
| 26 | 3-11 | DAC20 | 36.8 | 210.0 | 20.6 | 10.8 | 1.9 | Mass Spec. | 2320 |
| 27 | 3-1 | F | 31.0 | 189.0 | 23.5 | 12.2 | 1.9 | SFC | 299 |
| 28 | 3-4 | LCGO4 | 30.4 | 252.2 | 14.4 | 7.3 | 2.0 | UV | 13600 |
| 29 | 3-11 | DAC10 | 39.6 | 210.0 | 14.8 | 7 | 2.1 | Mass Spec. | 1200 |
| 30 | 3-4 | LCGO1 | 31.6 | 223.9 | 15.7 | 7.3 | 2.2 | UV | 14100 |
| 31 | 3-11 | TAC5 | 40.9 | 212.0 | 7.5 | 3.4 | 2.2 | Mass Spec. | 542 |
| 32 | 3-3 | G1 | 37.8 | | 22.1 | 9.7 | 2.3 | Unreported | ca. 500 |
| 33 | 3-3 | G6 | 32.2 | | 31.7 | 13.8 | 2.3 | Unreported | ca. 500 |
| 34 | 3-4 | LSLCO3 | 23.1 | 244.4 | 35.8 | 15.4 | 2.3 | UV | 0 |
| 35 | 3-7 | DD5 | 34.8 | 220.0 | 33.23 | 13.79 | 2.4 | HPLC IP391 | 1900 |
| 36 | 3-7 | DD4 | 34.8 | 220.0 | 33.87 | 14 | 2.4 | HPLC IP391 | 1900 |
| 37 | 3-2 | J4 | 37.2 | 206.0 | 24.7 | 10 | 2.5 | Unreported | 39 |
| 38 | 3-5 | A | 31.7 | 233.0 | 37.5 | 15.1 | 2.5 | HPLC IP391 | 2815 |
| 39 | 3-1 | A | 39.0 | 183.0 | 10.8 | 4.3 | 2.5 | SFC | 466 |
| 40 | 3-7 | DD11 | 35.4 | 225.0 | 30.14 | 11.86 | 2.5 | HPLC IP391 | 2900 |
| 41 | 3-4 | LCGO3 | 33.7 | 230.0 | 13.8 | 5.2 | 2.7 | UV | 10800 |
| 42 | 3-4 | LCO1 | 28.4 | 195.6 | 42.5 | 15.8 | 2.7 | UV | 1600 |
| 43 | 3-10 | N5 | 39.2 | | 26.5 | 9.8 | 2.7 | Unreported | ca. 5000 |
| 44 | 3-4 | LSLCGO6 | 31.2 | 314.4 | 11.4 | 4.2 | 2.7 | UV | 500 |
| 45 | 3-11 | LSC | 39.2 | 200.0 | 16.9 | 6.2 | 2.7 | Mass Spec. | 1300 |
| 46 | 3-4 | SRD1 | 42.2 | 170.0 | 12.3 | 4.5 | 2.7 | UV | 100 |

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| <u>Fuel #</u> | <u>Pub. #</u> | <u>Fuel Ref.</u> | <u>API Gravity</u> | <u>T10 °C</u> | <u>Aromatics wt. %</u> | <u>PNAs wt. %</u> | <u>Arom./ PNA</u> | <u>Anal. Test</u> | <u>S. wppm</u> |
|---------------|---------------|------------------|--------------------|---------------|------------------------|-------------------|-------------------|-------------------|----------------|
| 47 | 3-4 | LSLCO2 | 24.3 | 228.9 | 35.4 | 12.5 | 2.8 | UV | 0 |
| 48 | 3-11 | HSC | 37.8 | 221.0 | 22.1 | 7.6 | 2.9 | Mass Spec. | 9420 |
| 49 | 3-1 | Ref2 | 38.0 | 198.9 | 26.6 | 8.8 | 3.0 | HPLC | 351 |
| 50 | 3-9 | Fuel G | 34.3 | 214.0 | 33.9 | 11 | 3.1 | HPLC IP391 | 1000 |
| 51 | 3-9 | Fuel G1 | 34.3 | 214.0 | 33.9 | 11 | 3.1 | HPLC IP391 | 1000 |
| 52 | 3-9 | Fuel H1 | 34.3 | 214.0 | 33.9 | 11 | 3.1 | HPLC IP391 | 1000 |
| 53 | 3-9 | Fuel H | 36.8 | 199.0 | 24.4 | 7.9 | 3.1 | HPLC IP391 | 1000 |
| 54 | 3-9 | CS ADO 1 | 34.6 | 230.0 | 32.2 | 10.3 | 3.1 | HPLC IP391 | 380 |
| 55 | 3-3 | G5 | 36.9 | | 36.6 | 11.7 | 3.1 | Unreported | ca. 500 |
| 56 | 3-4 | LSLCGO5 | 32.5 | 266.7 | 11.2 | 3.5 | 3.2 | UV | 400 |
| 57 | 3-9 | Fuel E | 35.3 | 215.0 | 34.6 | 10 | 3.5 | HPLC IP391 | 800 |
| 58 | 3-4 | LALCO7 | 36.0 | 318.9 | 1.4 | 0.4 | 3.5 | UV | 0 |
| 59 | 3-2 | J5 | 39.6 | 206.0 | 17 | 4.7 | 3.6 | Unreported | 35 |
| 60 | 3-1 | C | 36.8 | 185.0 | 24.5 | 6.7 | 3.7 | SFC | 460 |
| 61 | 3-9 | Fuel F | 37.8 | 199.0 | 30.7 | 8.3 | 3.7 | HPLC IP391 | 800 |
| 62 | 3-9 | Fuel F1 | 37.8 | 199.0 | 30.7 | 8.3 | 3.7 | HPLC IP391 | 800 |
| 63 | 3-7 | DD12 | 33.4 | 236.0 | 25.93 | 6.95 | 3.7 | HPLC IP391 | 1700 |
| 64 | 3-4 | LSLCGO4 | 34.5 | 245.0 | 11 | 2.8 | 3.9 | UV | 200 |
| 65 | 3-11 | HDS | 39.6 | 217.0 | 24.2 | 6.1 | 4.0 | Mass Spec. | 445 |
| 66 | 3-9 | Ref | 37.0 | 207.0 | 25.8 | 5.7 | 4.5 | HPLC IP391 | 440 |
| 67 | 3-4 | LSLCGO0 | 35.7 | 219.4 | 10.5 | 2.3 | 4.6 | UV | 400 |
| 68 | 3-9 | Fuel A | 37.1 | 214.0 | 30.2 | 6.6 | 4.6 | HPLC IP391 | 600 |
| 69 | 3-9 | Fuel C | 36.9 | 216.0 | 28.5 | 6.2 | 4.6 | HPLC IP391 | 700 |
| 71 | 3-4 | LALCO6 | 31.1 | 286.1 | 2.5 | 0.5 | 5.0 | UV | 0 |
| 70 | 3-10 | N6 | 38.4 | | 25 | 5 | 5.0 | Unreported | ca. 5000 |
| 72 | 3-4 | LSLCO1 | 28.4 | 187.8 | 29.1 | 5.8 | 5.0 | UV | 100 |
| 73 | 3-10 | N4 | 42.5 | | 25.2 | 5 | 5.0 | Unreported | ca. 5000 |
| 74 | 3-1 | C10B | 41.7 | 207.5 | 10.2 | 2 | 5.1 | HPLC | 131 |
| 75 | 3-4 | LCGO2 | 36.9 | 201.7 | 11.4 | 2.2 | 5.2 | UV | 11600 |
| 76 | 3-1 | E | 31.0 | 183.0 | 25.2 | 4.8 | 5.3 | SFC | 374 |
| 77 | 3-1 | C30A | 37.9 | 198.5 | 29.6 | 5.6 | 5.3 | HPLC | 270 |
| 78 | 3-9 | Fuel B | 39.7 | 197.0 | 26.2 | 4.9 | 5.3 | HPLC IP391 | 500 |
| 79 | 3-10 | N3 | 39.0 | | 24.9 | 4.6 | 5.4 | Unreported | ca. 5000 |
| 80 | 3-9 | Fuel D | 39.4 | 196.0 | 25.2 | 4.6 | 5.5 | HPLC IP391 | 700 |
| 81 | 3-4 | LALCGO7 | 34.5 | 312.8 | 2.2 | 0.4 | 5.5 | UV | 0 |
| 82 | 3-4 | LASRD7 | 37.5 | 323.9 | 1.1 | 0.2 | 5.5 | UV | 0 |
| 83 | 3-10 | N7 | 39.2 | | 26.5 | 4.8 | 5.5 | Unreported | ca. 5000 |
| 84 | 3-3 | G7 | 42.6 | | 8.4 | 1.5 | 5.6 | Unreported | ca. 500 |
| 85 | 3-4 | LSLCGO3 | 36.9 | 222.2 | 10.2 | 1.8 | 5.7 | UV | 100 |
| 86 | 3-2 | J11 | 39.2 | 224.0 | 16.5 | 2.9 | 5.7 | Unreported | 23 |
| 87 | 3-2 | J12 | 36.8 | 231.0 | 13.2 | 2.3 | 5.7 | Unreported | 37 |
| 88 | 3-10 | N2 | 39.4 | | 25.5 | 4.4 | 5.8 | Unreported | ca. 5000 |
| 89 | 3-2 | J10 | 40.0 | 213.0 | 21.6 | 3.6 | 6.0 | Unreported | 75 |
| 90 | 3-1 | S10B | 38.1 | 183.0 | 12 | 2 | 6.0 | HPLC | 2 |
| 91 | 3-6 | D | 31.0 | 233.0 | 38.4 | 8.6 | 6.1 | MS 2425 | 510 |

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| <u>Fuel #</u> | <u>Pub. #</u> | <u>Fuel Ref.</u> | <u>API Gravity</u> | <u>T10 °C</u> | <u>Aromatics wt.%</u> | <u>PNAs wt.%</u> | <u>Arom./PNA</u> | <u>Anal. Test</u> | <u>S. wppm</u> |
|---------------|---------------|------------------|--------------------|---------------|-----------------------|------------------|------------------|-------------------|----------------|
| 92 | 3-6 | E | 37.6 | 233.0 | 38.4 | 8.6 | 6.1 | MS 2425 | 510 |
| 93 | 3-6 | F | 33.6 | 233.0 | 38.4 | 8.6 | 6.1 | MS 2425 | 510 |
| 94 | 3-7 | DD8 | 38.2 | 196.0 | 38.68 | 6.35 | 6.1 | HPLC IP391 | 300 |
| 95 | 3-11 | TNC5 | 42.3 | 213.0 | 6.1 | 1 | 6.1 | Mass Spec. | 2 |
| 96 | 3-9 | CS ADO 2 | 37.3 | 206.0 | 20.8 | 3.4 | 6.1 | HPLC IP391 | 130 |
| 97 | 3-9 | CS ADO 3 | 37.3 | 206.0 | 20.8 | 3.4 | 6.1 | HPLC IP391 | 140 |
| 98 | 3-1 | C20A | 40.8 | 191.0 | 20 | 3.2 | 6.3 | HPLC | 31 |
| 99 | 3-3 | G2 | 38.5 | | 18 | 2.8 | 6.4 | Unreported | ca. 500 |
| 100 | 3-11 | HCK | 44.1 | 179.0 | 6.7 | 1.04 | 6.4 | Mass Spec. | 50 |
| 101 | 3-2 | J1 | 37.4 | 216.0 | 27 | 4.1 | 6.6 | Unreported | 100 |
| 102 | 3-4 | LALCGO6 | 35.0 | 286.7 | 2.7 | 0.4 | 6.8 | UV | 0 |
| 103 | 3-1 | Ref1 | 37.7 | 205.6 | 25.9 | 3.6 | 7.2 | HPLC | 287 |
| 104 | 3-4 | LALCO5 | 30.3 | 267.8 | 2.9 | 0.4 | 7.3 | UV | 0 |
| 105 | 3-4 | LASRD6 | 38.7 | 297.2 | 1.5 | 0.2 | 7.5 | UV | 0 |
| 106 | 3-4 | LALCO4 | 31.0 | 247.2 | 3.9 | 0.5 | 7.8 | UV | 0 |
| 107 | 3-10 | N1 | 39.8 | | 27.4 | 3.5 | 7.8 | Unreported | ca. 5000 |
| 108 | 3-6 | I | 35.7 | 222.0 | 27.9 | 4.2 | 8.0 | MS 2425 | 420 |
| 109 | 3-11 | HDT40 | 41.1 | 214.0 | 16.9 | 2.1 | 8.0 | Mass Spec. | 2 |
| 111 | 3-1 | C20B | 40.4 | 194.0 | 19.8 | 2.4 | 8.3 | HPLC | 134 |
| 110 | 3-4 | LALCGO5 | 35.2 | 264.4 | 3.3 | 0.4 | 8.3 | UV | 0 |
| 112 | 3-5 | H(cut) | 35.8 | 234.1 | 8.5 | 1 | 8.5 | HPLC IP391 | 10 |
| 113 | 3-4 | LALCGO4 | 36.6 | 245.6 | 3.4 | 0.4 | 8.5 | UV | 0 |
| 114 | 3-4 | LASRD5 | 41.0 | 276.7 | 2.6 | 0.3 | 8.7 | UV | 0 |
| 115 | 3-4 | LALCO0 | 32.5 | 215.0 | 3.5 | 0.4 | 8.8 | UV | 0 |
| 116 | 3-6 | J | 35.4 | 228.0 | 25.6 | 3.6 | 8.9 | MS 2425 | 300 |
| 118 | 3-2 | J2 | 41.1 | 234.0 | 3.6 | 0.4 | 9.0 | Unreported | 1 |
| 117 | 3-4 | LASRD4 | 38.9 | 250.0 | 3.6 | 0.4 | 9.0 | UV | 0 |
| 119 | 3-1 | C30B | 39.4 | 198.5 | 30.2 | 3.3 | 9.2 | HPLC | 202 |
| 120 | 3-3 | G4 | 45.8 | | 15.7 | 1.7 | 9.2 | Unreported | ca. 500 |
| 121 | 3-3 | G3 | 40.5 | | 8.5 | 0.9 | 9.4 | Unreported | ca. 500 |
| 122 | 3-5 | H | 35.8 | 239.4 | 10.4 | 1.1 | 9.5 | HPLC IP391 | 10 |
| 123 | 3-8 | FSG | 40.5 | 218.5 | 14.8 | 1.5 | 9.9 | Unreported | 18 |
| 124 | 3-4 | LSLCGO2 | 39.0 | 203.9 | 10.9 | 1.1 | 9.9 | UV | 100 |
| 125 | 3-6 | A | 38.9 | 200.0 | 20 | 3.4 | 10.0 | MS 2425 | 410 |
| 126 | 3-6 | B | 38.9 | 200.0 | 20 | 3.4 | 10.0 | MS 2425 | 410 |
| 127 | 3-4 | LALCO3 | 31.6 | 230.0 | 4.1 | 0.4 | 10.3 | UV | 0 |
| 128 | 3-10 | N0 | 41.9 | | 25.7 | 1.1 | 23.4 | Unreported | ca. 5000 |
| 129 | 3-6 | L | 37.2 | 229.0 | 5.2 | 1.3 | 44.0 | MS 2425 | 490 |
| 130 | 3-5 | Ref. K541 | 40.0 | 216.7 | 9.8 | 0.8 | 12.3 | HPLC IP391 | 390 |
| 131 | 3-6 | K | 30.4 | 236.0 | 17.1 | 4.4 | 13.8 | MS 2425 | 110 |
| 132 | 3-6 | C | 40.7 | 198.0 | 11.7 | 1.6 | 16.9 | MS 2425 | 110 |
| 133 | 3-4 | LSLCGO1 | 41.4 | 182.2 | 10 | 0.6 | 16.7 | UV | 100 |
| 134 | 3-1 | S30An5 | 36.8 | 185.0 | 32.1 | 2.5 | 12.8 | HPLC | 85 |
| 135 | 3-1 | S30Bn1 | 37.3 | 186.5 | 31.3 | 2.5 | 12.5 | HPLC | 3 |
| 136 | 3-1 | S20Bn1 | 37.3 | 179.0 | 22.8 | 1.9 | 12.0 | HPLC | 31 |
| 137 | 3-1 | S20A | 38.2 | 181.0 | 20 | 1 | 20.0 | HPLC | 29 |
| 138 | 3-9 | CS ADO 4 | 41.2 | 202.0 | 19.8 | 1.4 | 14.1 | HPLC IP391 | 16 |

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| <u>Fuel #</u> | <u>Pub. #</u> | <u>Fuel Ref.</u> | <u>API Gravity</u> | <u>T10 °C</u> | <u>Aromatics, wt. %</u> | <u>PNAs, wt. %</u> | <u>Arom./PNA</u> | <u>Anal. Test</u> | <u>S, wppm</u> |
|---------------|---------------|------------------|--------------------|---------------|-------------------------|--------------------|------------------|-------------------|----------------|
| 139 | 3-2 | J7 | 45.6 | 192.0 | 1.8 | 0.05 | 36.0 | Unreported | 1 |
| 140 | 3-4 | LALCGO0 | 37.1 | 224.4 | 3.3 | 0.3 | 11.0 | UV | 0 |
| 141 | 3-4 | LASRD0 | 39.4 | 227.8 | 3.3 | 0.3 | 11.0 | UV | 0 |
| 142 | 3-4 | LALCGO3 | 38.5 | 225.0 | 3.5 | 0.3 | 11.7 | UV | 0 |
| 143 | 3-4 | LALCO2 | 32.6 | 211.1 | 3.6 | 0.2 | 18.0 | UV | 0 |
| 144 | 3-4 | LALCGO2 | 39.7 | 206.7 | 3.9 | 0.2 | 19.5 | UV | 0 |
| 145 | 3-11 | DNC20 | 41.5 | 206.0 | 4.1 | 0.2 | 20.5 | Mass Spec. | 1 |
| 146 | 3-1 | Ref3 | 36.6 | 244.8 | 4.2 | 0 | N.A. | HPLC | 9 |
| 147 | 3-4 | LALCGO1 | 41.0 | 190.0 | 4.5 | 0.2 | 22.5 | UV | 0 |
| 148 | 3-11 | DNC10 | 42.3 | 208.0 | 4.6 | 0.4 | 11.5 | Mass Spec. | 1 |
| 149 | 3-11 | TNC | 41.7 | 213.0 | 5 | 0.1 | 50.0 | Mass Spec. | 1 |
| 150 | 3-4 | LASRD3 | 37.6 | 226.7 | 5 | 0.4 | 12.5 | UV | 0 |
| 151 | 3-4 | LASRD1 | 47.8 | 116.1 | 7.7 | 0.1 | 77.0 | UV | 0 |
| 152 | 3-1 | C10A | 44.3 | 200.0 | 10.4 | 0.7 | 14.9 | HPLC | 8 |
| 153 | 3-6 | G | 44.2 | 172.0 | 14.2 | 1.3 | 12.1 | MS 2425 | 20 |
| 154 | 3-6 | H | 44.2 | 172.0 | 14.2 | 1.3 | 12.1 | MS 2425 | 20 |
| 155 | 3-11 | HDT70 | 43.0 | 211.0 | 6.6 | 0.5 | 13.2 | Mass Spec. | 1 |
| 156 | 3-4 | LASRD2 | 40.0 | 196.7 | 5.8 | 0.3 | 19.3 | UV | 0 |
| 157 | 3-1 | S10A | 39.6 | 175.5 | 11.7 | 0.5 | 23.4 | HPLC | 13 |
| 158 | 3-4 | LALCO1 | 35.4 | 183.3 | 5.6 | 0.2 | 28.0 | UV | 0 |

[0054] By using the diesel fuel compositions of the present invention in a compression ignition engine, the level of the pollutants NO_x and particulate matter is reduced. Accordingly, emissions levels of NO_x below 0.5g/Km and particulate matter below 0.05g/Km may be attained. These values/levels are significantly lower than that for comparable fuels in which the aromatic content split (i.e., the total aromatics to PNA ratio) falls outside the ranges of the present invention as shown in the examples below.

[0055] The present invention is further illustrated with reference to the Examples in Table 4.

[0056] The following data was generated from two distillate fuels. The first one, Example 4, was prepared in a commercial hydrodesulfurization unit from a virgin distillate feed using a conventional CoMo/Al₂O₃ catalyst and represents a typical commercial diesel fuel composition. The second one, Example 5, is a

composition according to the present invention. The properties of these two fuels are shown in Table 4 below.

Table 4

| | Example 4 | Example 5 |
|-------------------------------------|------------------|------------------|
| Sulfur (wppm) | 400 | 10 |
| Mono-aromatics (% wt) | 19.26 | 5.86 |
| Polynuclear aromatics (% wt) | 4.84 | 0.25 |
| Total aromatics (% wt) | 24.10 | 6.11 |
| Aromatics/PNAs | 5.0 | 24.44 |
| Density (kg/m³) | 844.1 | 832.3 |
| Cetane No. | 55.8 | 60 |
| T₉₅ (°C) | 337.0 | 335.2 |

- 5 **[0057]** These fuels were run in a fleet of 3 light-duty diesel vehicles encompassing traditional and modern technology, i.e., one with distributor pump technology, one with common rail fuel injection technology and one with electronic unit injector technology. Each fuel was tested three times in each vehicle (a total of nine tests per fuel) comprising a cold-start legislated European type certification
- 10 drive cycle (ECE + EUDC) in order to determine average particulate emissions and average NOx emissions for both fuels. These average values were then compared to the predicted values for both fuels in accordance with the European Programme on Emissions, Fuel and Engine (EPEFE) technologies and the AutoOil equation for the effect of sulfur to determine the expected performance of the fuels now used.
- 15 The EPEFE program is based on an established set of equations from testing of 11 diesel fuels in 19 vehicles to predict the emissions performance of a fleet of vehicles based upon the fuel parameters: cetane No., density and polycyclic aromatic content. On the basis of the differences in fuel parameters between Example 4 and Example 5, the EPEFE calculations would lead one to expect lower
- 20 particulate matter and NOx emissions for the fuel of Example 5.

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[0058] The results shown in Table 5 below show the average difference between the predicted reduction in emissions obtained from the EPEFE calculations and the observed reduction in average emissions for the fuel of Example 5 vs. the fuel of Example 4. Surprisingly, the data indicate that the reduction in NOx and particulate matter emissions achieved using the fuel compositions of the present invention (Example 5) were substantially greater than that predicted for any of the 19 vehicles used in the EPEFE program as well as being significantly lower than the EPEFE fleet average. In Table 5, negative percentages indicate an emissions performance improvement.

Table 5

EPEFE/AutoOil predictions and actual fleet measurements for Example 5 emissions vs. Example 4 emissions (%)

| EPEFE Vehicle | PM | NOx |
|-----------------------------|--------|-------|
| 1 | -10.1 | -0.1 |
| 2 | -12.0 | -0.1 |
| 3 | | 0.2 |
| 4 | -10.9 | |
| 5 | -5.7 | -1.7 |
| 6 | | -2.3 |
| 7 | -7.3 | -4.7 |
| 8 | -10.2 | -2.0 |
| 9 | -1.9 | -1.8 |
| 10 | -10.8 | 0.2 |
| 11 | -8.7 | 1.2 |
| 12 | -14.0 | -0.9 |
| 13 | -24.8 | -0.8 |
| 14 | -6.1 | -1.5 |
| 15 | -2.4 | -0.1 |
| 16 | -11.1 | -5.6 |
| 17 | -5.7 | -2.6 |
| 18 | -5.0 | -0.3 |
| 19 | -6.6 | -2.2 |
| EPEFE fleet prediction | -10.94 | -1.59 |
| Actual result from car test | -23.14 | -7.81 |

CLAIMS:

1. A distillate fuel composition boiling in the range of about 190°C to 400°C with a T10 point greater than 200°C, an API gravity less than 43, a sulfur level of less than about 50 wppm, a total aromatics content of about 5 to 15 wt.%, a polynuclear aromatics content of less than about 1.5 wt.%, wherein the ratio of total aromatics to polynuclear aromatics is greater than about 11.
2. The distillate fuel composition of claim 1 wherein the sulfur level is less than about 25 wppm.
3. The distillate fuel composition of claim 2 wherein the sulfur level is less than about 10 wppm.
4. The distillate fuel composition of claim 3 wherein the sulfur level is less than about 5 wppm.
5. The distillate fuel composition of claim 1 wherein the total aromatics content is from about 10 to 15 wt.%.
6. The distillate fuel composition of claim 1 wherein the polynuclear aromatics content is less than about 1.0 wt.%.
7. The distillate fuel composition of claim 6 wherein the polynuclear aromatics content is less than about 0.5 wt.%.
8. The distillate fuel composition of claim 1 wherein the ratio of total aromatics to polynuclear aromatics is greater than about 14.
9. The distillate fuel composition of claim 8 wherein the ratio of total aromatics to polynuclear aromatics is greater than about 17.

10. The distillate fuel composition of claim 5 wherein the sulfur level is less than about 25 wppm.
11. The distillate fuel composition of claim 10 wherein the sulfur level is less than about 10 wppm.
- 5 12. The distillate fuel composition of claim 11 wherein the sulfur level is less than about 5 wppm.
13. The distillate fuel composition of claim 6 wherein the sulfur level is less than about 25 wppm.
14. The distillate fuel composition of claim 13 wherein the sulfur level is less
10 than about 10 wppm.
15. The distillate fuel composition of claim 14 wherein the sulfur level is less than about 5 wppm.
16. The distillate fuel composition of claim 7 wherein the sulfur level is less than about 25 wppm.
- 15 17. The distillate fuel composition of claim 16 wherein the sulfur level is less than about 10 wppm.
18. The distillate fuel composition of claim 17 wherein the sulfur level is less than about 5 wppm.
19. The distillate fuel composition of claim 8 wherein the sulfur level is less than
20 about 25 wppm.
20. The distillate fuel composition of claim 19 wherein the sulfur level is less than about 10 wppm.

21. The distillate fuel composition of claim 20 wherein the sulfur level is less than about 5 wppm.
22. The distillate fuel composition of claim 9 wherein the sulfur level is less than about 25 wppm.
- 5 23. The distillate fuel composition of claim 22 wherein the sulfur level is less than about 10 wppm.
24. The distillate fuel composition of claim 23 wherein the sulfur level is less than about 5 wppm.
- 10 25. A distillate fuel composition boiling in the range of about 190°C to 400°C with a T10 point greater than 200 °C, an API gravity less than 43, a sulfur level of less than about 25 wppm, a total aromatics content of about 10 to 15 wt.%, a polynuclear aromatics content of less than about 1.0 wt.%, wherein the ratio of total aromatics to polynuclear aromatics is greater than about 14.
- 15 26. The distillate fuel composition of claim 25 wherein the sulfur level is less than about 10 wppm.
27. The distillate fuel composition of claim 26 wherein the sulfur level is less than about 5 wppm.
28. The distillate fuel composition of claim 25 wherein the polynuclear aromatics content is less than about 0.5 wt.%.
- 20 29. The distillate fuel composition of claim 25 wherein the ratio of total aromatics to polynuclear aromatics is greater than about 17.
30. The distillate fuel composition of claim 28 wherein the sulfur level is less than about 10 wppm.

31. The distillate fuel composition of claim 30 wherein the sulfur level is less than about 5 wppm.
32. The distillate fuel composition of claim 29 wherein the sulfur level is less than about 10 wppm.
- 5 33. The distillate fuel composition of claim 32 wherein the sulfur level is less than about 5 wppm.
34. An automotive distillate fuel composition boiling in the range of about 190°C to 400°C with a T10 point greater than 200°C, an API gravity less than 43, a sulfur level of less than about 10 wppm, a total aromatics content
10 of about 10 to 15 wt.%, a polynuclear aromatics content of less than about 0.5 wt.%, wherein the ratio of total aromatics to polynuclear aromatics is greater than about 17.
35. The distillate fuel composition of claim 34 wherein the sulfur level is less than about 5 wppm.
- 15 36. A method for abating particulate and NOx emissions in a compression ignition engine comprising providing to the engine a distillate fuel composition boiling in the range of about 190°C to 400°C with a T10 point greater than 200°C, an API gravity less than 43, a sulfur level of less than about 50 wppm, a total aromatics content of about 5 to 15 wt.%, a
20 polynuclear aromatics content of less than about 1.5 wt.%, wherein the ratio of total aromatics to polynuclear aromatics is greater than about 11.
37. A fuel composition comprising a distillate boiling in the range of about 190°C to 400°C with a T10 point greater than 200°C, an API gravity less than 43, a sulfur level of less than about 50 wppm, a total aromatics content
25 of about 5 to 15 wt.%, a polynuclear aromatics content of less than about 1.5

wt.%, wherein the ratio of total aromatics to polynuclear aromatics is greater than about 11, to which is added at least one of (i) one or more lubricity aid, (ii) one or more viscosity modifier, (iii) one or more antioxidant, (iv) one or more cetane improver, (v) one or more dispersant, (vi) one or more cold flow improver, (vii) one or more metals deactivator, (viii) one or more corrosion inhibitor, (ix) one or more detergent, and (x) one or more distillate or upgraded distillate.

FIGURE 1

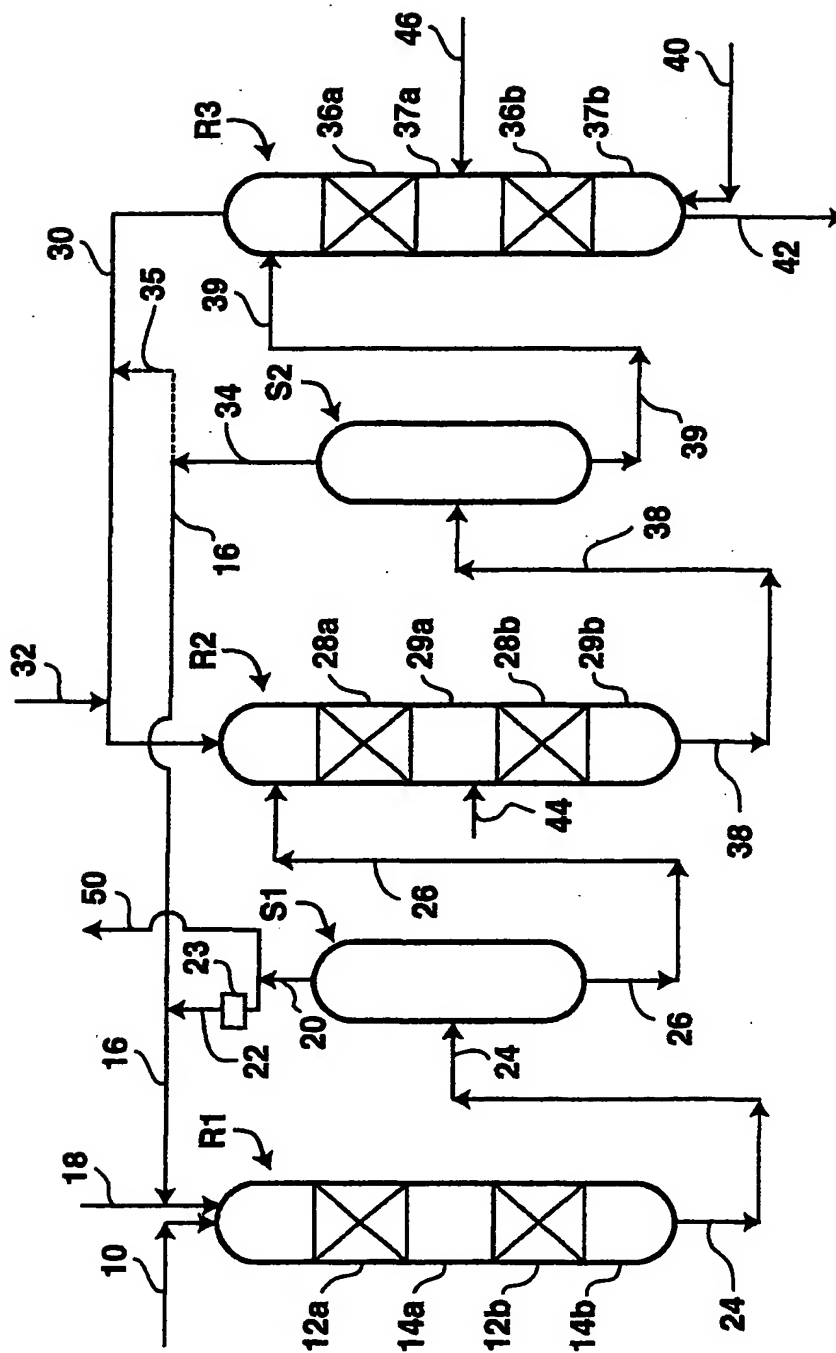
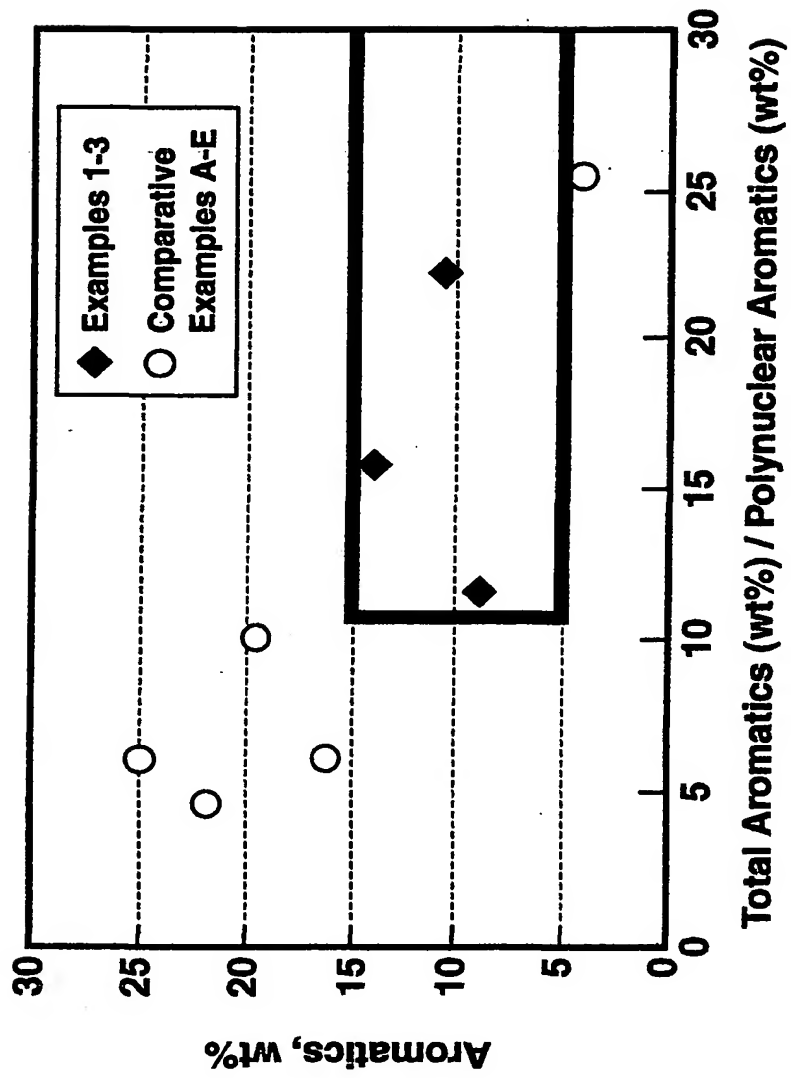


FIGURE 2



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